NANOTECHNOLOGICAL AND SYNTHETIC MODIFICATIONS ONTO CELLULOSE FOR THE REMEDIATION OF TRIVALENT AND HEXAVALENT CHROMIUM FROM WATER BODIES: A GREEN NANOTECHNOLOGICAL PERSPECTIVE

A
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INTRODUCTION

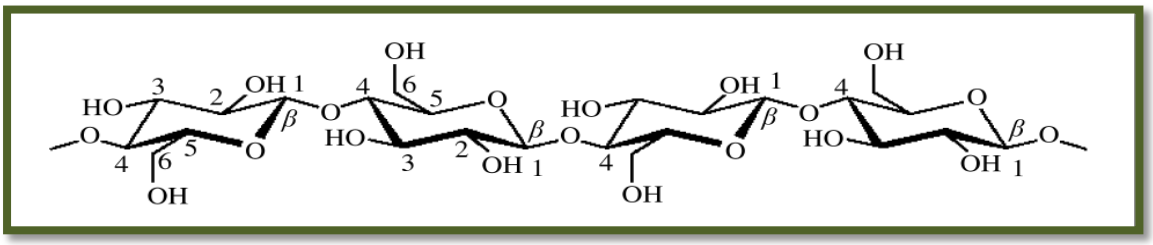
The ability of water is of vital concern for mankind since it is directly linked with human welfare. Among the various pollutants encountered in water, toxic metals are highly important because of their non biodegradable nature and long biological half life which ultimately cause them to accumulate in various ecosystems of the environment. Among various toxic metals, Chromium, released in the various effluents from tanneries and electroplating units situated in Agra, the city of Taj Mahal is highly important from its environmental pollution point of views. It is a unique element giving its paradoxyl role in both nutrition and carcinogenesis. It exists in two environmentally important oxidation states: trivalent and hexavalent Chromium. Trivalent Chromium is considered essential for carbohydrate metabolism. However, trivalent Chromium at higher concentration has also been found associated with toxicity issues ***(Rakhunde et al., 2013)***. Hexavalent Chromium is soluble anion and has been placed in first quartile of 53 compounds evaluated by **Cancer Assessment Group (CAG)**. The toxicity of hexavalent form of Chromium to the living cells and essentiality of its trivalent form in human nutrition are opposing concern to make this element an area of sustained research. The toxicological, physiological and geochemical behaviours depend upon the oxidation state of the metal. The toxicity of any metal (Chromium) does not depend on the total metal concentration rather on the concentration of particular metal oxidation state (Cr VI) exhibiting toxicity. Therefore, chemical speciation of Chromium and its removal from water bodies has been really a challenging task for environmentalists even today.

The conventional methods such as flocculation, electrolysis, precipitation, ion exchange membrane technologies, reverse osmosis and crystallization used for abatement of toxic metals are often restricted because of several technical, economical and environmental constraints. Further, abatement of metals in the above processes has been largely attempted using inorganic agents which have been again established for toxicity issues.

The emerging concept of **"Clean Production and Process"** is a new principle guiding the next generation products and processes**.** To combine technology with environmental safety is one of the key challenges of the new millennium ***(Hoque et al., 2006)*****.** There is a global trend of bringing technology into harmony with natural environment, thus aiming to achieve the goals of protection of ecosystem from the potentially deleterious effects of human activity and finally improving its quality. The challenges of treating and diagnosing environmental problems require discovery of newer, more potent, specific, safe and cost effective synthetic or natural or semi synthetic molecules. The magic plants/products/wastes are around and waiting to be discovered and commercialized.

Bioremediation: A green solution to pollution reduces overall treatment cost through the application of biomaterial which is particularly attractive as they lessen reliance on expensive water treatment chemicals, negligible transportation requirements and offer genuine, local resources as appropriate solutions to tackle local issues of water quality. **Regeneration** of biomaterials increases the cost effectiveness of the process thus, warrants its future success. Use of plant materials with an aim to effectively alleviate the economic aspects allowing, further extension of water supply to rural areas of developing countries. Bioremediation of toxic metals from aqueous system is defined as the ability of local organic resources (agricultural wastes) to bind metals from waste water through metabolically mediated physico-chemical pathways of sorption. It provides an appropriate solution to tackle the issues of water quality problems. However, biomaterials recently have been reported to have certain limitations of less sorption efficacy, environmental stability and workability for cationic metal species mainly, restricting their commercial use. **Green nano technology** integrates nanotechnology and environmental chemistry generating a significant option forward in bio sorption process whose efficacy mainly depends on the size of particles of organic sorbents. Organo nanoparticles can easily be engineered with important functional groups to increase affinity towards both cationic and anionic target metal species. The complexity of organic materials represents the achievements of structural order of many length scales with full structure developed from the nested levels of structural hierarchy in which self assembled organic materials can form templates.

Cellulose, among various explored bio sorbents, is an almost inexhaustible polymeric raw material with fascinating structure and properties ***(Abdel-Halim et al., 2012, Coseria et al., 2012).*** It is formed by repeated connection of D-glucose building blocks. It is a large linear polymer with a large number of hydroxyl groups (3 per a hydro glucose pyranose unit) present in the preferred in $^{4}C_{1}$ conformation.



This molecular structure gives cellulose, characteristic properties of hydrophilicity, chirality, reactivity, biodegradability and broad chemical modifying capacity ***(Peng et al., 2011, Habibi, 2014).*** Its formation of versatile semicrystalline fibres morphology due to sensitivity toward the hydrolysis and oxidation of the chain forming acetal groups, which determine its chemistry and handling, environmental friendly and biocompatible material. Chemical reactivity towards cationic species is largely a function of the high donor reactivity of the OH groups. However, on the basis of structure of crystalline cellulose, there is no cationic centre in the cellulose for the sorption of anionic species.

Enrichment of functional groups responsible for anionic metal binding on cellulose molecule, making it suitable sorbent for the removal of cationic and anionic metal species from aqueous system.

Current research is oriented towards the structural modifications onto the biomaterials leading to the enhancement of binding capacity; selectivity and environmental stability in terms of their reusability are, therefore in great demands. The implementation of the local environment tactics of achieving the environment goals in a localized region of environment is green strategy and the need of the day.

PRESENT STATE OF KNOWLEDGE IN THE AREA OF RELEVANCE

A vigorous survey of the literature on the topic at International and National level has been conducted and presented in a concise manner. The survey indicates the following pattern of growth of research on the subject. Different bio sorbents for Chromium removal have been listed below:

Table: 1 Bio sorbents Used so far for Chromium Removal

S. N.	Adsorbents	Maximum adsorption capacity $Q_{m\ (mg/g)}$	References
1.	Peanut hull	84.20	*Brown et al., 2000*
2.	Hazelnut shell	142.32	*Cimino et al., 2000*
3.	Oil Palm	08.62	*Guo &Lua, 2000*
4.	*Rhizopus nigricans*	09.64	*Sudha & abrahm, 2001*
5.	Fly ash	03.24	*Rao et al., 2002*
6.	Composite chitosan	153.80	*Boddu et al., 2003*
7.	*Aeromonas cerviae*	124.50	*Loukidou et al.,2004*
8.	Potato peel waste	89.90	*Ahalya et al., 2005*
9.	Saltbush plant	09.45	*Sawalha et al., 2005*
10.	Chitosan	17.86	*Nomanbhay & Palanisamy, 2005*
11.	Ulmus leaves	49.87	*Gholami et al., 2006*
12.	Eucalyptus bark	45.00	*Sarin & Pant et al., 2006*
13.	Coconut husk	12.50	*Amuda et al., 2007*
14.	Oak saw dust	89.40	*Argunet al., 2007*
15.	Hazelnut shell	153.25	*Bulut &Tez, 2007*
16.	Yellow passion fruit	85.10	*Jacques et al., 2007*
17.	Maize cob	56.45	*Mahvi et al., 2007*
18.	*Rhizopus arrhizus*	81.45	*Preetha & Viruthagiri, 2007*
19.	Wheat bran	40.80	*Sun et al., 2008*
20.	*Zea mays*	07.63	*Goyal et al., 2009*
21.	Rose waste	04.69	*Iftikhar et al.,2009*
22.	Groundnut hull	31.54	*Qaiser et al., 2009*
23.	*Moringa oliefera*	12.62	*Ghebremichael et al., 2010*
24.	Sunflower waste	14.84	*Jain et al., 2010*
25.	Coconut sawdust	10.20	*Ting et al., 2010*
26.	Coconut coir	04.56	*Talokar, 2011*
27.	Peanut shell	09.87	*Krowiak et al., 2011*
29	Hemicellulose	02.30	*Lin and Wang, 2012*
30.	Eggshell	88.46	*Daraei et al., 2013*
31.	Cow Hooves	89.00	*Osasona et al., 2013*
32.	Sugarcane bagasse	37.30	*Sharma & Sharma,2013*
33.	Sheesham sawdust	67.10	*Sharma & Sharma,2013*
34.	Eggshell	94.50	*Rubcumintara, 2014*

Nanotech enforcement onto cellulose

Nanocellulose, as a new generation of nano-scale material from forest products, has received considerable attention ***(Wegner and Jones 2006; Eichhorn et al., 2010; Habibi et al., 2010; Siqueira et al., 2010; Moon et al., 2011; Klemm et al., 2011)***. Nanomaterials derived from renewable biomaterials, especially cellulose and lignocelluloses, will undoubtedly play a large role in the nanotechnology research effort**.** Nanocellulose is a kind of natural green resource. A polymer composed of cellulose nanofibers 1-100 nm ***(Korotkov et al., 2012)*** whose functional properties are determined by the fibril structure is called nanocellulose**.**

Lima and Borsali, 2004 described the principle of the disruption of the amorphous regions of cellulose in order to produce cellulose nanocrystals. The hydronium ions can penetrate the material in these amorphous domains promoting the hydrolytic cleavage of the glycosidic bonds releasing individual crystallites. ***Beck-Candanedo et al., 2005*** studied the properties of cellulose nanocrystals obtained by hydrolysis of softwood and hardwood pulps. They studied the influence of hydrolysis time and acid-to-pulp ratio in order to obtain cellulose nanocrystals. ***Bondeson et al., 2006*** optimised the reaction conditions for sulfuric acid hydrolysis of microcrystalline cellulose (MCC). The concentration of MCC and sulfuric acid, hydrolysis time, temperature and ultrasonic treatment time were varied during the process. It was found that the reaction time, temperature and acid concentration were critical factors for the production of nanocrystalline cellulose (NCC). ***Wang et al., 2007*** studied a combination of both sulfuric and hydrochloric acids during hydrolysis steps appear to generate spherical nanocrystals under ultrasonic conditions. ***Hafraoui et al., 2008*** studied the effect of temperature on the size distribution of nanocrystalline cellulose (NCC) produced from sulfuric acid hydrolysis of cotton, and they demonstrated that shorter NCC was obtained by increasing the temperature. ***Rinaldi & Schüth, 2009*** concluded concentrated sulfuric acid has the capability of hydrolyzing cellulose chains by interacting rapidly with the glycosidic oxygen linking two sugar units in a cellulose chain. ***Lu & Hsieh, 2010*** studied the acid hydrolysis and freeze-drying of cotton cellulose in order to produce nanocrystals with rod, sphere, and network structured morphologies. The results demonstrated that the acid hydrolysis not only produced nanocrystalline structures but also introduced surface charges for their effective separation. ***Sadeghifar et al., 2011*** studied the effect of hydrobromic acid concentration, and different reaction parameters in order to obtain cellulose nanocrystals. ***Ioelovich, 2012*** studied the effect of sulfuric acid concentration, acid/cellulose ratio, temperature and treatment time, as well as disintegration conditions and to optimize preparation process of nanocrystalline cellulose particles. ***Lu et al., 2013*** studied the preparation, characterization and optimization of nanocellulose whiskers from filter papers by sulfuric acid hydrolysis simultaneously ultrasonic wave and microwave assisted.

Table: 2 Functionalization onto Cellulose/ Nanocellulose

Type of modifications	Modification reagents	References
Grafting on nanocellulose	Poly(ethylene glycol)	*Araki et al., 2001*
Grafting on cellulose	Acrylic Polymers	*Margutti et al., 2002*
Grafting on nanocellulose	Styrene	*Yi et al.,2008*
Grafting on nanocellulose	Azobenzene polymers	*Xu et al., 2008*
Grafting on nanocellulose	Polycaprolactone	*Habibi, 2008*
Grafting on nanocellulose	*N*,*N*-dimethylaminoethylmethacrylate	*Morandi et al., 2009*
Grafting on cellulose	Poly(methacrylic acid)	*Tian et al., 2010*
Grafting on cellulose	Poly(methacrylic acid)	*Anirudhan et al., 2011*
Grafting on nanocellulose	Tetraethylenepentamine	*Donia et al., 2012*
Grafting on nanocellulose	Poly glycidylmethacrylate	*Anirudhan et al.,2012*
Grafting on cellulose	Radiation-induced styrene	*Zhang et al., 2012*
Grafting on nanocellulose	Acrylamide	*Yang et al., 2012*
Grafting on hemicellulose	Penetic acid	*You et al., 2013*
Esterification on cellulose	Propanetricarboxylic acid	*Sungur, 2005*
Esterification on cellulose	Vinyl esters	*Cao et al.,2013*
Esterification on nanocellulose	Phosphate Ester	*Heux et al.,2000*
Esterification on nanocellulose	Alkyenyl Succinic anhydride (ASA)	*Yuan et al.,2006*
Esterification on nanocellulose	Palmitoyl chloride	*Berlioz et al., 2009*
Esterification on nanocellulose	Fischer process	*Braun & Dorgan, 2009*
Esterification on nanocellulose	Maleic anhydride	*Tanq et al., 2013*
Esterification on mercerized nanocellulose	Succinic anhydride	*Hokkanen et al., 2013*
Amination on cellulose	Polyallylamine	*Kim et al., 2002*
Amination on cellulose	Didecyl dimethyl ammonium chloride (DDAC)	*Liu et al., 2014*
Amination on nanofibers	Polyaniline	*Zheng et al., 2012*
Oxidation on nanocellulose	Tetramethylpiperidine-1-oxyl (TEMPO)	*Habibi et al., 2006*
Oxidation on nanocellulose	Tetramethylpiperidine-1-oxyl (TEMPO)	*Salajkova et al.,2012*
Radiation on nanocellulose	5-isothiocyanate (FITC)	*Dong & Roman, 2007*
Thiolation on cellulose	Aminoethanethiol	*Silva et al., 2013*
Phosphorylation on cellulose	Phosphoric acid	*Rungrodnimitchai,2014*

HIGHLIGHTS OF THE LITERATURE SURVEY

The detailed survey of literature indicates following important points:

- Abatement of toxic metals has been largely attempted using inorganic and organic bio sorbents, but none have reached to the commercial level.
- Chemical speciation of toxic metals has been carried out using costly chemical reagent and not much attention has been paid on the use of economical plant materials.
- Nanocellulose displays a high concentration of hydroxyl groups at the surface than cellulose which can easily be functionalized with various chemical modifying reagents to increase their affinity towards target species.
- Special emphasis is required to nanotech enforcement for enhance sorption efficacy and environmental stability of cellulose making them viable for commercial use.
- The potential of chemically modified biomaterials for cationic metal species has been explored. Information on the ability of chemically modified bionanomaterials to remove anionic metal species from aqueous system is highly restricted.
- The tributary river Yamuna is frequently polluted by majority of toxic heavy metals. Concentration of Chromium level continuously increases above the permissible limit (0.1mg/ml).

OBJECTIVES

The present work addresses the nanotech enforcement and functionalization onto cellulose leading to the preparation of smart biomaterial with enhanced **sorption efficacy, environmental stability, ability of chemical speciation and removal** of trivalent (Cr III) and hexavalent (Cr VI) species from water bodies.

PLAN OF WORK

The work would be carried out with following specific aims:

A. NANOTECH ENFORCEMENT

Nanotech enforcement onto cellulose to obtain the cellulose nanocrystals under following experimental conditions:

- Nature and concentration of hydrolysing agents
- Acid to cellulose ratio
- Reaction time and temperature

B. FUNCTIONALIZATIONS

(a) Functionalization onto cellulose nanocrystals for the introduction of COO^- and $:NH_2$ centre for the binding of cationic trivalent form of Chromium such as:

Graft co-polymerization with

- glycidylmethacrylate [GMA] followed by poly (acrylic) acid [PAA]
- glycidylmethacrylate [GMA] followed by tetraethylenepentamine [TEPA]

Chelation with

- 4-hydroxy benzoic acid

(b) Functionalization onto cellulose nanocrystals for the introduction of positively charged amino centre for the binding of anionic hexavalent form of Chromium such as:

Graft co-polymerization with

- polyethylenimine [PEI]
- poly aniline [PAN]

Cationization with

- epoxy propyl trimethyl ammonium chloride [EPTMAC]

C. CHARACTERIZATION OF FUNCTIONALIZED CELLULOSE NANOCRYSTALS

Using following analytical techniques:

- Fourier transform infrared spectroscopy, FTIR
- Scanning electronic microscopy, SEM
- Atomic force microscopy, AFM
- BET surface area

D. OPTIMIZATION OF STANDARD CONDITIONS FOR MAXIMUM SORPTION OF CATIONIC AND ANIONIC CHROMIUM SPECIES ONTO CELLULOSE NANOCRYSTALS/ FUNCTIONALIZED CELLULOSE NANOCRYSTALS

Batch experiments as functions of:

- pH
- Biosorption dose
- Concentration of metal species
- Contact time
- Initial volume

E. REUSABILITY OF CHROMIUM LOADED CELLULOSE NANOCRYSTALS/ FUNCTIONALISED CELLULOSE NANOCRYSTALS

In order to design the proposed method of decontamination of Chromium, more economical, a series of sorption and desorption batch experiments would be conducted by eluting the biomass with following acids:

- Mineral acids
- Organic acids

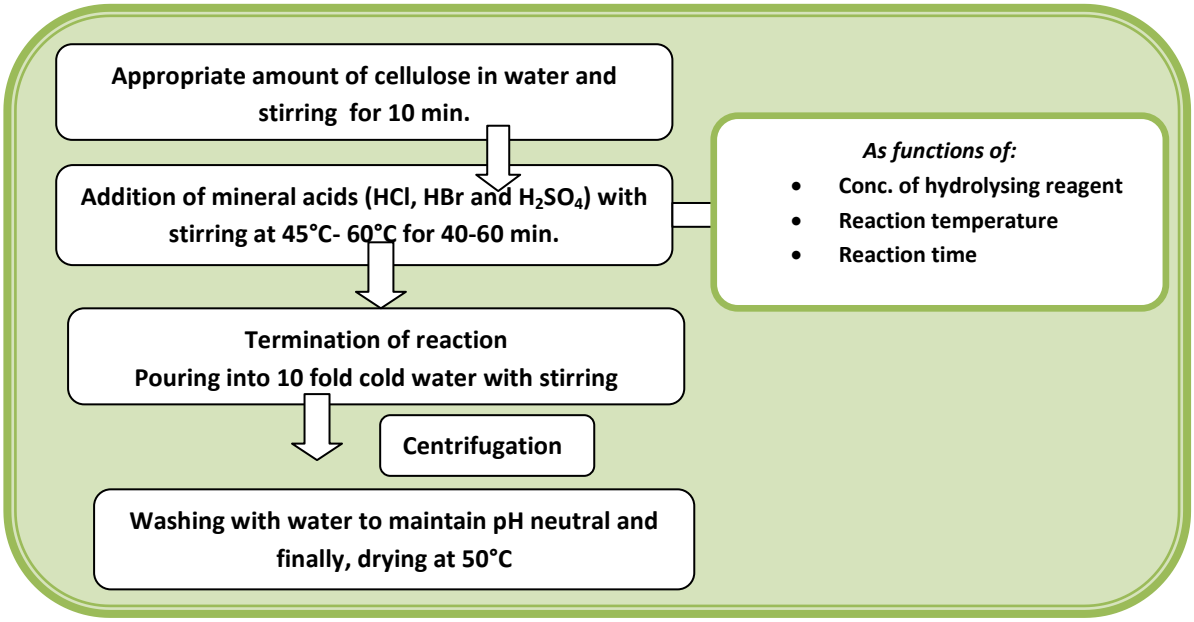
F. APPLICABILITY OF THE METHOD TO THE ENVIRONMENTAL SAMPLES

The proposed method would be assessed for its efficacy in terms of percentage of removal of trivalent and hexavalent species of Chromium in tannery effluent. Electro analytical method (Anodic Stripping Voltammetry) and or Atomic Absorption Spectrometry (Difference method) would be attempted for the speciation of trivalent and hexavalent Chromium.

METHODS AND METHODOLOGY

Plan of work is depicted schematically as follows:

A. NANOTECH ENFORCEMENT ONTO CELLULOSE TO OBTAIN THE CELLULOSE NANOCRYSTALS

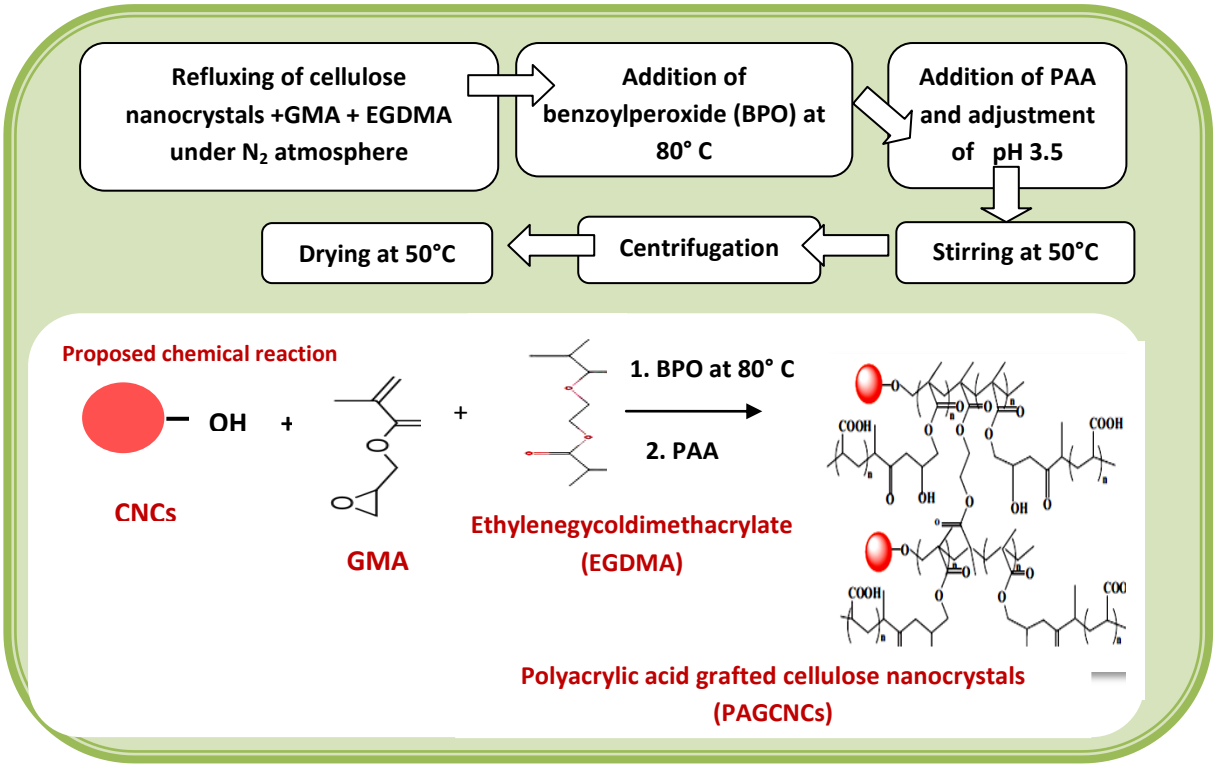

Appropriate amount of cellulose in water and stirring for 10 min.
Addition of mineral acids (HCl, HBr and H_2SO_4) with stirring at 45°C- 60°C for 40-60 min.
As functions of:
Conc. of hydrolysing reagent
Reaction temperature
Reaction time
Termination of reaction
Pouring into 10 fold cold water with stirring
Centrifugation
Washing with water to maintain pH neutral and finally, drying at 50°C

B. FUNCTIONALIZATIONS

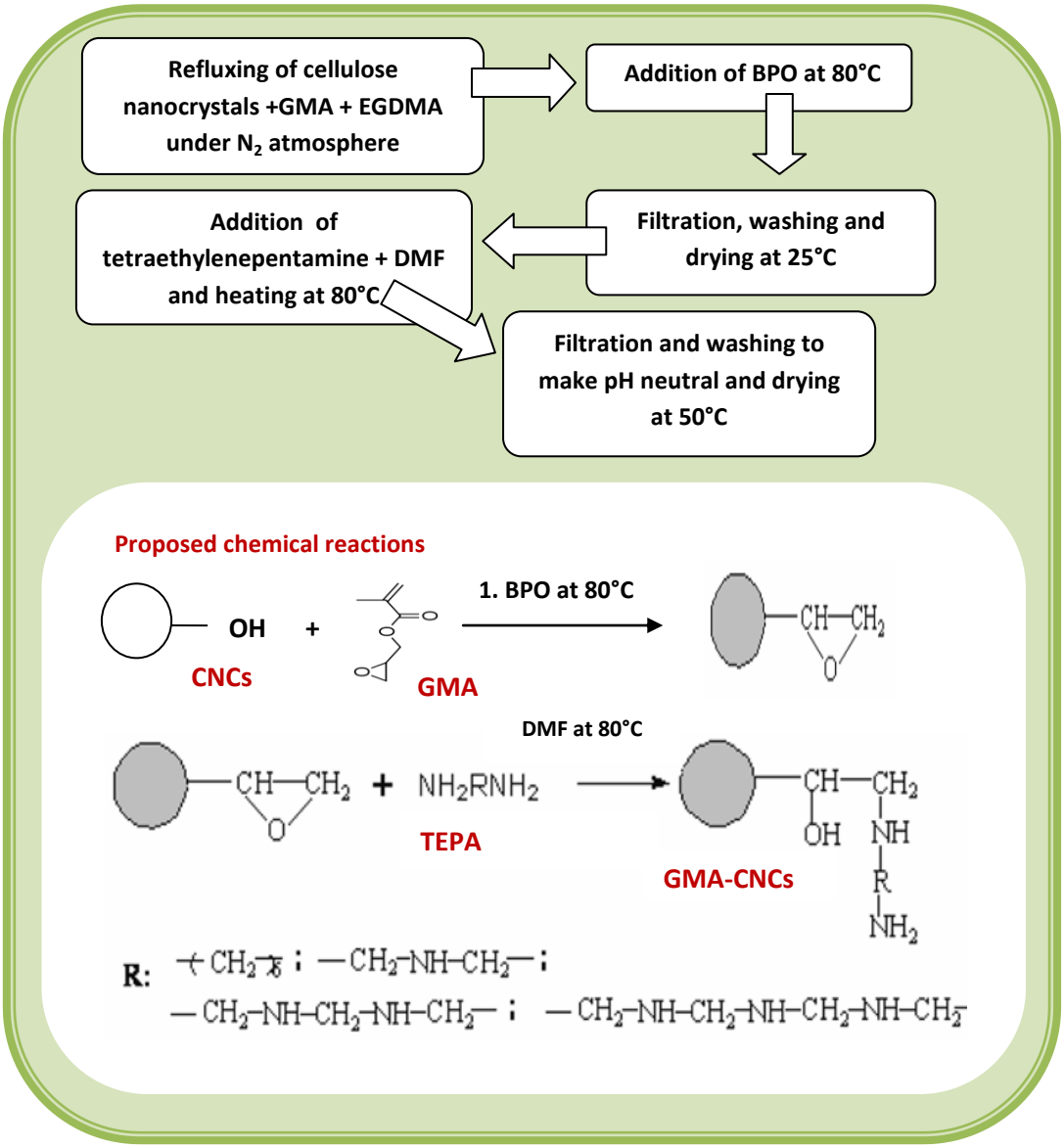
(a) Functionalization onto cellulose nanocrystals for the introduction of COO^- and $:NH_2$ centre for the binding of cationic trivalent form of Chromium:

GRAFT CO-POLYMERIZATION WITH

- glycidylmethacrylate [GMA] followed by poly (acrylic) acid [PAA]

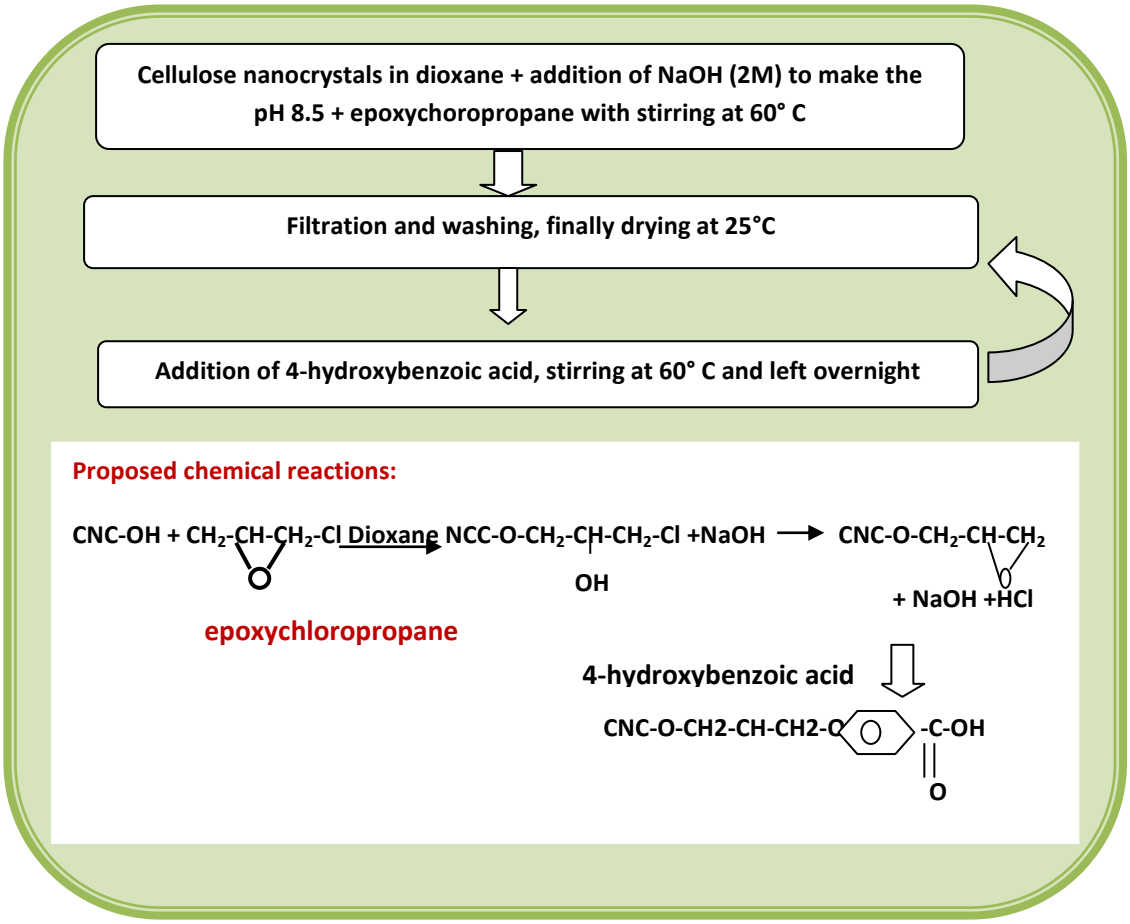


- glycidylmethacrylate [GMA] followed by tetraethylenepentamine [TEPA]


Refluxing of cellulose nanocrystals +GMA + EGDMA under N_2 atmosphere
Addition of BPO at 80°C
Filtration, washing and drying at 25°C
Addition of tetraethylenepentamine + DMF and heating at 80°C
Filtration and washing to make pH neutral and drying at 50°C
Proposed chemical reactions
OH
CNCs
GMA
1. BPO at 80°C
DMF at 80°C
TEPA
GMA-CNCs
R:

CHELATION WITH

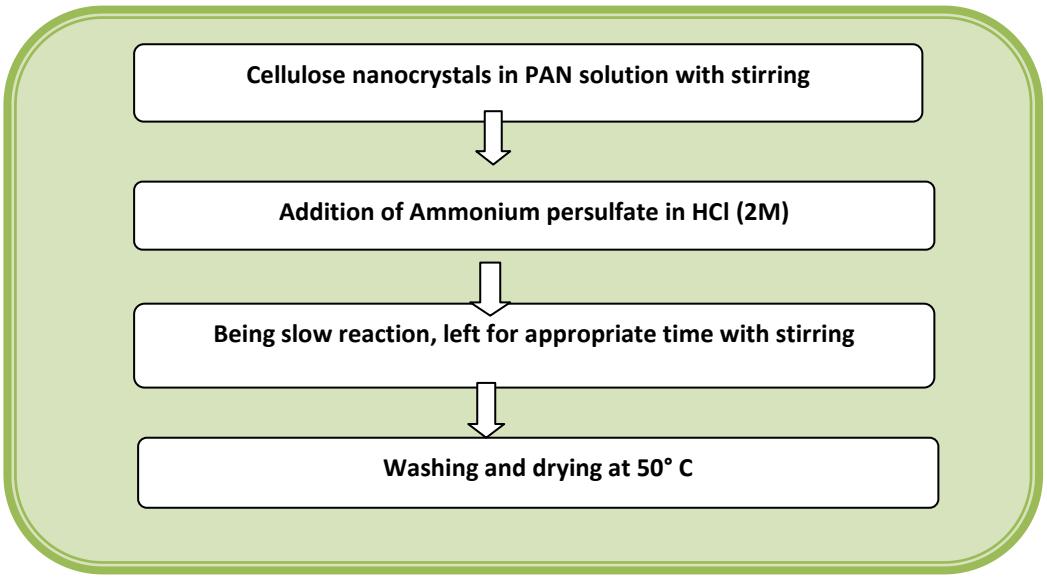
- 4-hydroxybenzoic acid


Cellulose nanocrystals in dioxane + addition of NaOH (2M) to make the pH 8.5 + epoxychoropropane with stirring at 60° C
Filtration and washing, finally drying at 25°C
Addition of 4-hydroxybenzoic acid, stirring at 60° C and left overnight
Proposed chemical reactions:
CNC-OH + CH2-CH-CH2-Cl Dioxane NCC-O-CH2-CH-CH2-Cl +NaOH
OH
CNC-O-CH2-CH-CH2
+ NaOH +HCl
epoxychloropropane
4-hydroxybenzoic acid
CNC-O-CH2-CH-CH2-C
-C-OH
O

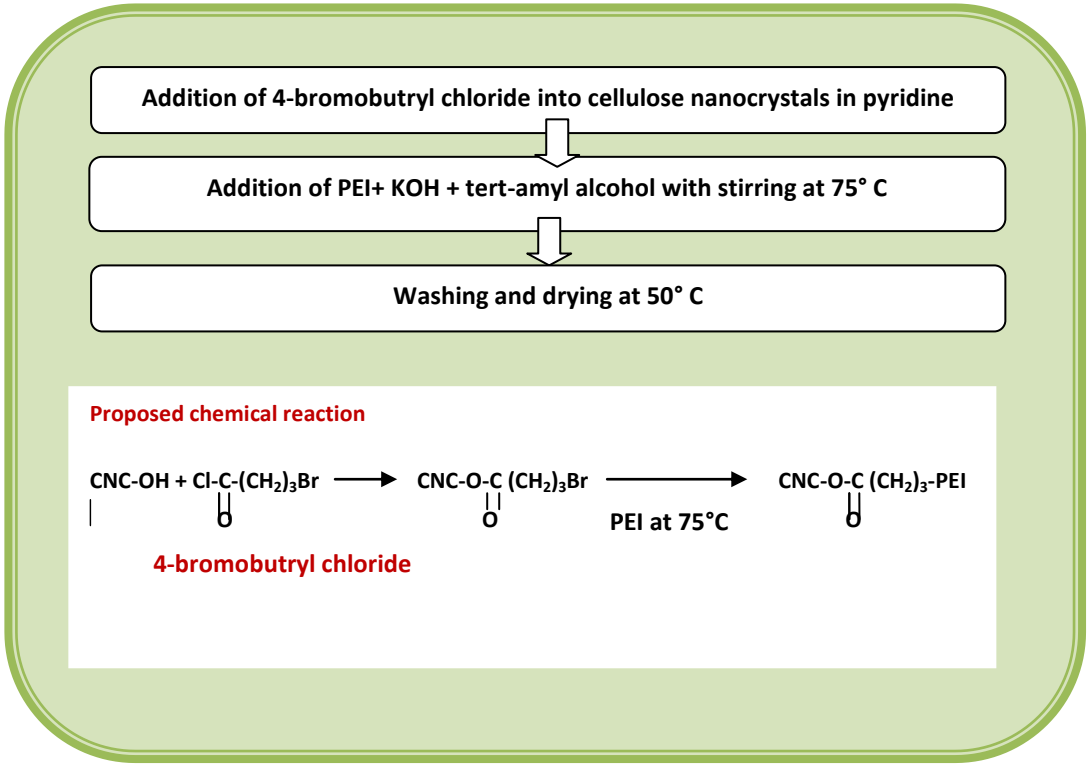
(b) Functionalization onto cellulose nanocrystals for the introduction of positively charged amino centre (NH^+) for the binding of anionic hexavalent form of chromium such as:

GRAFT CO-POLYMERIZATION WITH

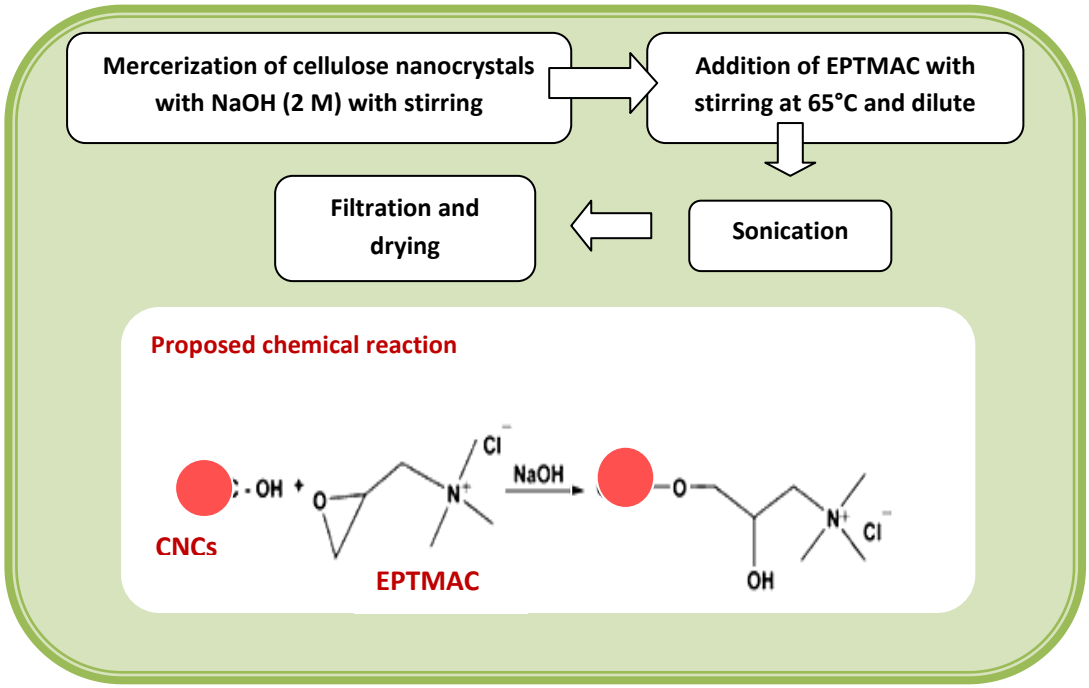
- Poly aniline [PAN]


Cellulose nanocrystals in PAN solution with stirring
Addition of Ammonium persulfate in HCl (2M)
Being slow reaction, left for appropriate time with stirring
Washing and drying at 50° C

- polyethylenimine [PEI]

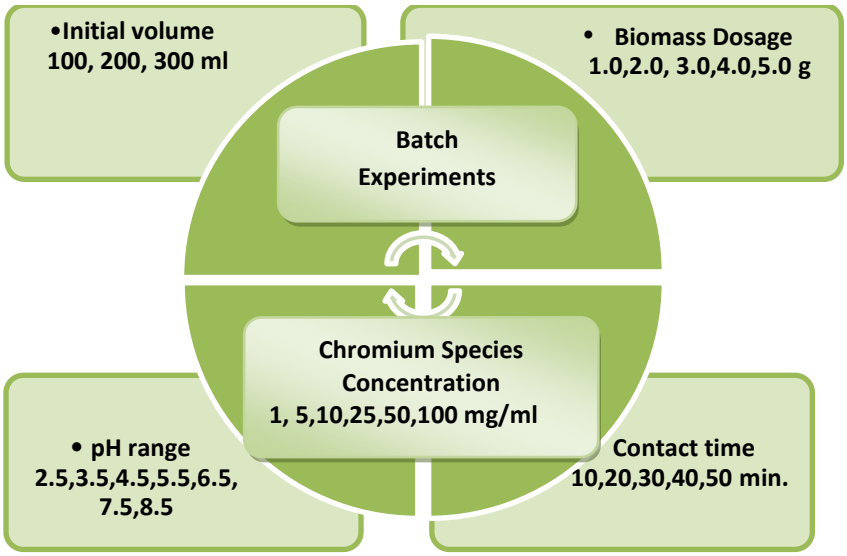

Addition of 4-bromobutryl chloride into cellulose nanocrystals in pyridine
Addition of PEI+ KOH + tert-amyl alcohol with stirring at 75° C
Washing and drying at 50° C
Proposed chemical reaction
CNC-OH + Cl-C-(CH2)3Br
CNC-O-C (CH2)3Br
PEI at 75°C
CNC-O-C (CH2)3-PEI
4-bromobutryl chloride

CATIONIZATION WITH EPTMAC

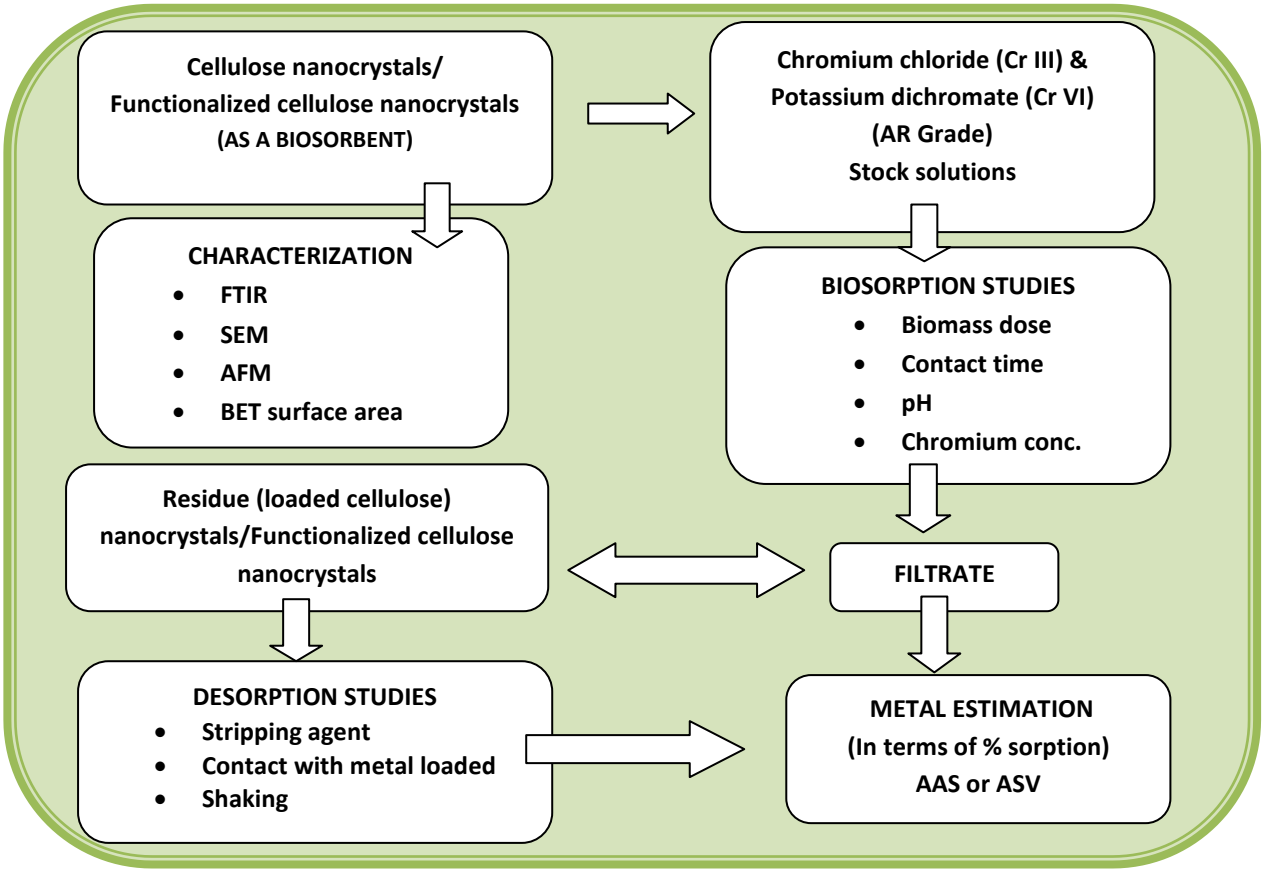


C. EXPERIMENTAL CONDITIONS FOR SORPTION

Sorption efficacy at laboratory scale using standard practices would be carried out in batch experiments under various experimental conditions



D. STANDARDIZATION AND CHARACTERIZATION OF CHROMIUM SPECIES, CELLULOSE NANOCRYSTALS/FUNCTIONALIZED CELLULOSE NANOCRYSTALS INTERACTION FOR THE EVALUATION OF SORPTION AND REGENERATION EFFICIENCY



SIGNIFICANCE OF WORK

The use of designed **Smart Biomaterials** (Functionalized cellulose nanocrystals) with enhanced sorption potential, environmental stability and ability of chemical speciation is deemed to be a strong foundation for the development of low cost, domestic and eco friendly method for remediation of cationic Cr III and anionic Cr VI species of Chromium from water bodies for rural and remote areas, particularly, for Agra which has number of industries releasing Chromium in their effluent. The proposed method could be a potential challenge for conventional existing methods.

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